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in Mechanics of Materials

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ON THE ROLE OF THE SECOND LAW OF THERMODYNAMICS
IN MECHANICS OF MATERIALS

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ABSTRACT   This lecture summarizes the recent work of Green and Naghdi
[1,2] concerning the thermomechanics of dissipative materials,
the main features of which are: (a) The introduction of a con-
servation law for entropy which holds for all materials,
(b) the use of the energy equation as an identity for all
processes, thereby leading to restrictions on constitutive
equations, and (c) the development of an inequality representing
a mathematical interpretation of a statement of the second law
of thermodynamics.

1.   Introduction

This is an expository account of a new approach to the thermo-
mechanics of dissipative materials proposed in two recent papers by
Green and Naghdi [1,2]. Although this approach already has been extended
to mixtures of interacting continua [3] and to nonlocal elasticity [4],
we confine attention here to classical single phase continua and quote
freely from the contents of [1,2].

In the context of single phase continuum mechanics, a number of dif-
ferent approaches are currently in use for treating the thermomechanical
behavior of dissipative materials and especially for imposing on constitu-
tive equations restrictions demanded by an appropriate form of the second
law of thermodynamics. A prominent approach to the subject utilizes the
Clausius-Duhem inequality (hereafter referred to as C-D inequality) in
the manner proposed by Coleman and Noll [5]. Although the latter proce-
dure has yielded acceptable results in important special cases, the C-D
inequality has been the subject of much criticism in recent years, for
example by Rivlin [6], by Day [7] and by Green and Naghdi [1,2]. In
general the criticisms stem from two main factors: (1) It is not at all
clear how the basic ideas contained in the statement of the second law of
thermodynamics have been translated into the C-D inequality and (2) the
inability of the C-D inequality to rule out unacceptable behavior in
some materials.

After recalling the conservation laws of the purely mechanical

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theory (section 2), thermal properties and conservation laws of the thermomechanical theory are discussed in section 3. These conservation laws, in addition to the balance of energy (the first law of thermodynamics), include a balance of entropy in the form introduced in [1]. A procedure for the utilization of these conservation laws is outlined (section 3) and involves the use of the energy equation as an identity for all motions and all temperature distributions (after the elimination of the external fields) and leads to restrictions on constitutive equations. This is illustrated in the case of an elastic material which is taken to be <u>nondissipative</u> in a sense that is later made precise. Expressions for external mechanical work and heat calculated in section 4 are then employed in section 5 to obtain a mathematical interpretation of a statement of the second law representing the notion that in a dissipative medium it is impossible to reverse completely a process in which mechanical energy is transformed into heat. We conclude this review by mentioning in section 6 certain additional features of the approach to thermomechanics proposed in [1,2].

2. Conservation laws in a mechanical theory.

Consider a finite body $\mathcal{B}$ with material points X and identify the material point X with its position $\underset{\sim}{\mathbf{X}}$ in a fixed reference configuration. A motion of the body is defined by a sufficiently smooth vector function $\underset{\sim}{\chi}$ which assigns position $\underset{\sim}{x} = \underset{\sim}{\chi}(\underset{\sim}{X},t)$ to each material point X at each instant of time t. In the present configuration at time t, the body $\mathcal{B}$ occupies a region of space $\mathcal{R}$ bounded by a closed surface $\partial\mathcal{R}$. Similarly, in the present configuration, an arbitrary subset $\mathcal{S}$ ($\subseteq\mathcal{B}$) of the body $\mathcal{B}$ occupies a part $\mathcal{P}$ ($\subseteq\mathcal{R}$) of the region $\mathcal{R}$, bounded by a closed surface $\partial\mathcal{P}$.

Let $\rho = \rho(\underset{\sim}{X},t)$ be the mass density in the present configuration and designate the velocity vector at time t by $\underset{\sim}{v} = \dot{\underset{\sim}{x}}$, where a superposed dot denotes material time derivative. We assume the existence of an external body force $\underset{\sim}{b} = \underset{\sim}{b}(\underset{\sim}{X},t)$ per unit mass acting on the body $\mathcal{B}$ in the present configuration and an internal surface force $\underset{\sim}{t} = \underset{\sim}{t}(\underset{\sim}{X},t\,;\underset{\sim}{n})$, called the stress vector, acting on the boundary[2] $\partial\mathcal{P}$ with outward unit normal $\underset{\sim}{n}$. The rate of work by these forces are, respectively, $\underset{\sim}{b}\cdot\underset{\sim}{v}$ per unit mass and $\underset{\sim}{t}\cdot\underset{\sim}{v}$ per unit area.

We adopt the usual conservation equations for mass, momentum and moment of momentum for every material part $\mathcal{S}\subseteq\mathcal{B}$ occupying a region $\mathcal{P}\subseteq\mathcal{R}$ and denote the elements of volume and area in the present configuration by dv and da, respectively. Thus, we write

$$\frac{d}{dt}\int_{\mathcal{P}}\rho\,dv = 0 \quad , \tag{1}$$

$$\frac{d}{dt}\int_{\mathcal{P}}\rho\,\underset{\sim}{v}\,dv = \int_{\mathcal{P}}\rho\,\underset{\sim}{b}\,dv + \int_{\partial\mathcal{P}}\underset{\sim}{t}\,da \quad , \tag{2}$$

$$\frac{d}{dt}\int_{\mathcal{P}}\rho\underset{\sim}{x}\times\underset{\sim}{v}\,dv = \int_{\mathcal{P}}\rho\underset{\sim}{x}\times\underset{\sim}{b}\,dv + \int_{\partial\mathcal{P}}\underset{\sim}{x}\times\underset{\sim}{t}\,da \tag{3}$$

with corresponding local forms

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[2] Of course, when $\mathcal{P}=\mathcal{R}$, $\underset{\sim}{t}$ assumes the value of the external traction on the surface $\partial\mathcal{R}$.

$$\dot{\rho} + \rho \operatorname{div} \underset{\sim}{v} = 0 \quad ,$$

$$\operatorname{div} \underset{\sim}{T} + \rho \underset{\sim}{b} = \rho \dot{\underset{\sim}{v}} \quad , \quad \underset{\sim}{t} = \underset{\sim}{T} \underset{\sim}{n} \quad , \tag{4}$$

$$\underset{\sim}{T}^T = \underset{\sim}{T} \quad .$$

In (4), $\underset{\sim}{T}$ is the Cauchy stress tensor, $\underset{\sim}{T}^T$ its transpose, and div stands for the divergence operator with respect to the place $\underset{\sim}{x}$.

3. Thermal properties of the body. Conservation laws in a thermo-mechanical theory.

We consider now the thermal properties of the body. The absolute temperature at each material point is represented by a scalar field $\theta = \theta(\underset{\sim}{X}, t) > 0$. We also admit the existence of:

$r = r(\underset{\sim}{X}, t) =$ external rate of supply of heat per unit mass;

$-h = -h(\underset{\sim}{X}, t \; ; \underset{\sim}{n}) =$ internal heat flux across the surface $\partial \mathcal{P}$ and measured per unit area of the surface $\partial \mathcal{P}$ per unit time[3].

We define the quantities $s = s(\underset{\sim}{X}, t)$ and $k = k(\underset{\sim}{X}, t \; ; \underset{\sim}{n})$ by

$$s = \frac{r}{\theta} \quad , \quad k = \frac{h}{\theta} \tag{5}$$

and call these, respectively, the external rate of supply of entropy per unit mass and the internal surface flux of entropy across $\partial \mathcal{P}$ per unit area of $\partial \mathcal{P}$ per unit time[4]. Also, throughout the body, we assume the existence of the scalar fields:

$\eta = \eta(\underset{\sim}{X}, t) =$ entropy per unit mass;

$\xi = \xi(\underset{\sim}{X}, t) =$ internal rate of production of entropy per unit mass;

$\epsilon = \epsilon(\underset{\sim}{X}, t) =$ internal energy per unit mass.

For a body susceptible to both mechanical and thermal effects, the conservation laws (1)-(3) are supplemented by the balance of entropy

$$\frac{d}{dt} \int_{\mathcal{P}} \rho \, \eta \, dv = \int_{\mathcal{P}} \rho(s + \xi) dv - \int_{\partial \mathcal{P}} k \, da \tag{6}$$

introduced in [1] and the balance of energy

$$\frac{d}{dt} \int_{\mathcal{P}} \rho(\tfrac{1}{2} \underset{\sim}{v} \cdot \underset{\sim}{v} + \epsilon) dv = \int_{\mathcal{P}} \rho(r + \underset{\sim}{b} \cdot \underset{\sim}{v}) dv + \int_{\partial \mathcal{P}} (\underset{\sim}{t} \cdot \underset{\sim}{v} - h) da \quad , \tag{7}$$

representing the first law of thermodynamics. Both (6) and (7) hold for an arbitrary part $\mathcal{S} \subseteq \mathcal{B}$ in the present configuration.

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[3] When $\mathcal{P} = \mathcal{R}$, the heat flux h assumes its value on the external boundary surface $\partial \mathcal{R}$.

[4] These terminologies associated for s and k arise naturally from consideration of the special case of a gas or an inviscid fluid mentioned later in this section, following Eq. (11).

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By usual procedures and under suitable continuity assumptions, the equations resulting from (6) and (7) are:

$$\rho\dot{\eta} = \rho(s+\xi) - \text{div } \underset{\sim}{p} \quad , \quad k = \underset{\sim}{p} \cdot \underset{\sim}{n} \quad ,$$

$$-\rho(\dot{\epsilon}-\theta\dot{\eta}) + \underset{\sim}{T} \cdot \underset{\sim}{D} - \rho\xi\theta - \underset{\sim}{p} \cdot \underset{\sim}{g} = 0 \quad , \tag{8}$$

where $\underset{\sim}{p}$ is the entropy flux vector, $\underset{\sim}{D} = \frac{1}{2}(\underset{\sim}{L}+\underset{\sim}{L}^T)$ is the rate of deformation tensor, $\underset{\sim}{L} = \text{grad } \underset{\sim}{v}$, $\underset{\sim}{g} = \text{grad } \theta$, grad denotes the gradient operator with respect to $\underset{\sim}{x}$ keeping t fixed and the term $\rho\xi\theta$ in $(8)_3$ is the contribution of ξ to the internal rate of production of heat. From $(5)_2$ and $(8)_2$, $h = \theta\underset{\sim}{p} \cdot \underset{\sim}{n}$ and we may define the heat flux vector $\underset{\sim}{q}$ by

$$\underset{\sim}{q} = \theta\underset{\sim}{p} \quad . \tag{9}$$

Introducing the Helmholtz free energy $\psi = \psi(\underset{\sim}{X},t)$ per unit mass by

$$\psi = \epsilon - \theta\eta \quad , \tag{10}$$

the energy equation $(8)_3$ may be written in the alternative form

$$-\rho(\dot{\psi}+\eta\dot{\theta}) + \underset{\sim}{T} \cdot \underset{\sim}{D} - \rho\xi\theta - \underset{\sim}{p} \cdot \underset{\sim}{g} = 0 \quad . \tag{11}$$

At this point, it is worth making some observations regarding the conservation equations $(8)_{1,3}$. First, we note that in the special case of a gas or an inviscid fluid and starting only with the energy equation and appropriate constitutive equations, it can be demonstrated that two scalar functions θ, η exist such that an equation of the form $(8)_1$ holds with s and k given by $(5)_{1,2}$ and with $\rho\theta\xi = -\underset{\sim}{p} \cdot \underset{\sim}{g}$. This result serves in part as the motivation for the balance equation (6) which is postulated to hold for all materials. Second, we have excluded a discussion of jump conditions at a surface of discontinuity. It should, however, be noted that the internal rate of production of entropy ξ may become unbounded on a surface of discontinuity in such a way that the volume integral of ξ in (6) contributes to the jump condition (see Green and Naghdi [8]). Third, a more primitive form of balance of energy involves an internal rate of production of energy. In order to deny the possibility that combined thermal and mechanical energy can continually be extracted from the body in closed cycles of deformation and temperature, the internal rate of production of energy is expressed as the time derivative of an internal energy density ϵ. See, in this connection, Green and Naghdi [9, p. 42] and [10, p. 356].

It is customary to regard the temperature θ as an independent thermodynamical variable. Thus, for a given body (having a reference mass density $\rho_0(\underset{\sim}{X})$), the field equations obtained from the integral forms of the conservation laws involve a set of 9 functions. These consist of the deformation function $\underset{\sim}{\chi}$ and the temperature θ, i.e.,

$$\{\underset{\sim}{\chi},\theta\} \tag{12}$$

and the various mechanical and thermal fields, namely[5]

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[5]The mass density ρ is not included in (13) and (14) since, given (12), ρ can be calculated from the equation for conservation of mass.

$$\{\underset{\sim}{T}, \underset{\sim}{p}, \psi, \eta, \xi\} \tag{13}$$

and

$$\{\underset{\sim}{b}, s\} \ . \tag{14}$$

We assume that the fields (13) are specified by constitutive equations which may depend on the variables (12), their space and time derivatives, as well as the whole history of deformation and temperature. We then adopt the following procedure in utilizing the conservation laws:

    (i) The field equations are assumed to hold for an arbitrary choice of the functions (12) including, if required, an arbitrary choice of the space and time derivatives of these functions;

    (ii) The fields (13) are calculated from their respective constitutive equations;

    (iii) The values of $\underset{\sim}{b}$ and s can then be found from the balance of linear momentum $(4)_2$ and the balance of entropy $(8)_1$;

    (iv) The equation $(4)_4$ resulting from the balance of moment of momentum and the equation $(8)_3$ resulting from the balance of energy will be regarded as identities for every choice of (12). These will then place restrictions on the constitutive equations.

We note that the quantities ξ, η, ψ may be arbitrary to the extent of additive functions $\hat{f}, f, -\theta f$, respectively, where f is an arbitrary function of the variables (12), their space and time derivatives and functionals of their histories. The additive functions have the property that they make no contribution to the differential equations for the variables (12) and the boundary and initial conditions. They also make no contribution to the energy identity (11) and no contribution to the internal energy ϵ. We reduce this arbitrariness by setting[6]

$$f = \hat{f}(\underset{\sim}{X}) \quad , \quad \dot{f} = 0 \ . \tag{15}$$

Then the function ξ is determined uniquely and η is only arbitrary to the extent of an additive function of $\underset{\sim}{X}$, independent of t. The function $\hat{f}$ in $(15)_1$ can thus be determined by specifying a value for η in some reference state. For example, in the case of an elastic medium, we may choose $\hat{f}$ in $(15)_1$ to be a constant value so that η is a constant η_0 corresponding to a constant reference temperature if the reference state is homogeneous.

Before closing this section, we apply the foregoing procedure to a discussion of thermomechanical behavior of elastic materials. An elastic material is defined by specifying constitutive equations for the fields (13) as functions of the variables

$$\{\underset{\sim}{F}, \theta, \underset{\sim}{g}\} \quad ,$$

where $\underset{\sim}{F} = \partial \underset{\sim}{X}/\partial \underset{\sim}{X}$ is the deformation gradient and the possible dependence on $\underset{\sim}{X}$ indicating inhomogeneity is understood. After imposing the usual invariance requirements under superposed rigid body motions of the whole body, the constitutive equation for the Helmholtz free energy reduces to

$$\psi = \overline{\psi}(\underset{\sim}{C}, \theta, _0\underset{\sim}{g}) \quad , \tag{16}$$

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[6]For details, see [1, Sec. 2].

where $C = F^T F$ and $_o g = F^T g$, with similar constitutive results for η, T, ξ, p. Next, we introduce (16) along with corresponding constitutive equations into the energy equation (11) and demand (by (iv) of section 3) that the latter, as well as $(4)_4$, be identically satisfied for every choice of the variables[7] (12). This leads to

$$\{T - \rho F(\frac{\partial \bar{\psi}}{\partial C} + \frac{\partial \bar{\psi}}{\partial C^T})F^T\} \cdot D - \rho(\eta + \frac{\partial \bar{\psi}}{\partial \theta})\dot{\theta} - \rho \frac{\partial \bar{\psi}}{\partial _o g} \cdot _o \dot{g} - \rho \xi \theta - p \cdot g = 0 \quad , \quad (17)$$

where $\dot{C} = 2F^T D F$. For given values of the variables which occur in the argument of $\bar{\psi}$ in (16), we may choose $D, \dot{\theta}, _o\dot{g}$ arbitrarily; and since the coefficients of $D, \dot{\theta}$ and $_o\dot{g}$ in (17) are independent of these rate quantities, we conclude that $\partial\bar{\psi}/\partial _o g = 0$ and then deduce that

$$\psi = \hat{\psi}(C,\theta) \quad , \quad \eta = -\frac{\partial \hat{\psi}}{\partial \theta} \quad , \quad T = \rho F(\frac{\partial \hat{\psi}}{\partial C} + \frac{\partial \hat{\psi}}{\partial C^T})F^T \tag{18}$$

and

$$\rho \xi \theta = - p \cdot g \quad . \tag{19}$$

Clearly (18) and (19), in addition to being necessary, are also sufficient conditions for the satisfaction of $(4)_4$ and (11) as identities for all motions and all temperature distributions. With the use of (19), (5) and (9), $(8)_1$ reduces to

$$\rho r - \text{div } q = \rho \theta \dot{\eta} \tag{20}$$

for an elastic material. The results (18) and (20) are, of course, the same as those found by Coleman and Noll [5] using the C-D inequality. Here, however, no appeal has yet been made to a second law of thermodynamics.

The results (18)-(20) include those for an inviscid fluid when the dependence of the fields (13) on C is assumed to occur through det C or equivalently through the mass density ρ.

4.   External supplies of mechanical work and heat.

Preliminary to the discussion of the second law, we need to record the expressions for the external mechanical work and the external heat supplied to a material part $S \subseteq \mathcal{B}$ during the time interval $\mathcal{J} = [t_1, t_2]$ in the present configuration. First, however, we observe that in the case of an elastic material the response functions for ψ, η, ϵ depend only on the deformation gradient F and the temperature θ and are independent of their rates and the temperature gradient g. Such an elastic material will be regarded as nondissipative in a sense that will be made precise later; and, in conjunction with an expression for the external mechanical work supplied to any part P, will be used as a basis for establishing later an inequality representing the second law of thermodynamics for dissipative materials Keeping this background in mind, we assume that the constitutive response functions for ϵ, η include also dependence on the list of variables F, θ, g and their higher space and time derivatives and refer to this list collectively as $\mathcal{V}$. Further, let ϵ', η' denote the respective values of ϵ, η when the set $\mathcal{V}$ is put equal to zero in the

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[7]Recall (iii) of section 3.

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response functions[8]. Thus, for example,

$$\epsilon = \epsilon(\underset{\sim}{F},\theta,\upsilon) \quad , \quad \epsilon' = \epsilon'(\underset{\sim}{F},\theta) = \epsilon(\underset{\sim}{F},\theta,0) \quad ,$$

$$\upsilon = (\dot{\underset{\sim}{F}},\dot{\theta},\underset{\sim}{g},\dots) \quad , \tag{21}$$

where the dots in $(21)_3$ refer to the higher space and time derivatives of $\underset{\sim}{F},\theta,\underset{\sim}{g}$. Then, with the help of (4) and the integral of (7) with respect to time, we obtain

$\mathbb{W}$ = External mechanical work supplied to a part $\mathcal{S}$ of the body during the time interval $\vartheta = [t_1,t_2]$

$$= \int_{\vartheta} W(\mathcal{P})dt = \Delta K(\mathcal{P}) + \Delta E(\mathcal{P}) + \overline{\mathbb{w}} + \mathbb{w}_2 \tag{22}$$

and

$\mathbb{H}$ = External heat supplied to a part $\mathcal{S}$ of the body during the time interval $\vartheta = [t_1,t_2]$

$$= \int_{\vartheta} Q(\mathcal{P})dt = - [\overline{\mathbb{w}} + \mathbb{w}_2] \quad , \tag{23}$$

where the prefix Δ denotes the "difference" operation on functions and fields during the time interval ϑ, e.g., $\Delta K = K(t_2) - K(t_1)$. Also, in (22) and (23) the functions W,K,E and Q representing the rate of work by body and surface forces, the kinetic energy, the internal energy and the total external supply of heat, respectively, are defined by

$$W(\mathcal{P}) = \int_{\mathcal{P}} \rho \underset{\sim}{b} \cdot \underset{\sim}{v} \, dv + \int_{\mathcal{P}} \underset{\sim}{t} \cdot \underset{\sim}{v} \, da \quad ,$$

$$K(\mathcal{P}) = \int_{\mathcal{P}} \tfrac{1}{2}\rho \underset{\sim}{v} \cdot \underset{\sim}{v} \, dv \quad , \quad E(\mathcal{P}) = \int_{\mathcal{P}} \rho \epsilon \, dv \quad , \tag{24}$$

$$Q(\mathcal{P}) = \int_{\mathcal{P}} \rho r \, dv - \int_{\partial\mathcal{P}} \underset{\sim}{q} \cdot \underset{\sim}{n} \, da \quad ,$$

the quantities $\overline{\mathbb{w}}$ and $\mathbb{w}_2$ are

$$\overline{\mathbb{w}} = -\int_{\vartheta}\int_{\mathcal{P}} \rho\theta\dot{\eta}' dv \, dt \quad , \quad \mathbb{w}_2 = \int_{\vartheta}\int_{\mathcal{P}} \rho w^* dv \, dt \tag{25}$$

and

$$\rho w^* = \rho\theta\dot{\eta}' - (\rho r - \operatorname{div} \underset{\sim}{q})$$

$$= \rho[w - (\dot{\epsilon}-\dot{\epsilon}')]$$

$$= -\rho(\dot{\epsilon}-\theta\dot{\eta}') + \underset{\sim}{T} \cdot \underset{\sim}{D} \quad , \tag{26}$$

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[8] These definitions of ϵ',η' do not exclude their dependence on the past histories of $\underset{\sim}{F},\theta,\underset{\sim}{g}$ (see section 6 of [1]).

$$\rho w = -\rho(\dot{\psi}' + \eta'\dot{\theta}) + \underset{\sim}{T} \cdot \underset{\sim}{D}$$
$$= \rho[\dot{\psi} - \dot{\psi}' + (\eta - \eta')\dot{\theta}] + \rho\xi\theta + \underset{\sim}{p} \cdot \underset{\sim}{g} \quad , \tag{27}$$

where $\psi' = \epsilon' - \theta\eta'$. It is clear from $(26)_2$ that in situations where ϵ does not depend on the list of variables $(21)_3$, then $\epsilon = \epsilon'$ and w^* becomes identical to w.

In the case of an elastic material, since the function $\hat{\psi}$ in $(18)_1$ is independent of the variables υ in $(21)_3$, it is clear that $\psi = \psi'$, $\eta = \eta'$ (and hence $\epsilon = \epsilon'$). Moreover, in this case, by virtue of (19) and $(27)_2$, we also have $w \equiv 0$. Thus, for an elastic material $w^* = 0$ and $w_2 = 0$ by $(25)_2$. We make use of this latter result in the next section and regard the elastic body, which has the value zero for w_2, as a reference (or "yard-stick") from which the dissipation of mechanical energy into heat is calculated.

5. The second law of thermodynamics. Restrictions on heat conduction vector and internal energy.

In the first law it is assumed that mechanical energy can be changed into heat energy and conversely, and no restriction is placed on the transformation of one into the other. It appears to be a fact of experience that whereas the transformation of mechanical energy into heat, for example through friction, is not limited by any restrictions, the reverse transformation, namely that of heat into mechanical energy, is subject to definite limitations. This fact has been incorporated into a number of different statements, each of which is then usually called the second law of thermodynamics. It is often asserted that the various statements of the second law are equivalent although proofs of this are far from convincing and usually limited to special situations. For example, a form of second law attributed to Kelvin (1851) is[9]:

(A) It is impossible to construct an engine which would extract heat from a given source and transform it into mechanical energy, without bringing about some additional changes in the bodies taking part. A slight variant of this statement which involves periodic cycles is due to Planck and is known as the Kelvin-Planck statement of the second law.

Another form of the second law is:

(B) It is impossible completely to reverse a process in which energy is transformed into heat by friction.

There are other statements of similar character such as that due to Carathéodory. A somewhat different idea seems to be involved in the form of the second law attributed to Clausius (1850):

(C) Heat cannot pass spontaneously from a body of lower temperature to a body of higher temperature.

A statement such as (C) does not necessarily involve the concept of mechanical work since it could be applied to rigid heat conducting solids, but many books contain "proofs" that (C) is equivalent to (A) or (B).

Although the first two of the above statements convey the ideas that some restrictions must be placed on the interchangeability of energy due

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[9]The various versions of the second law are recalled here as statements (A), (B) and (C). These or variants thereof can be found in standard books on thermodynamics, e.g., Schmidt [11], Zemansky [12] and Pippard [13].

to heat and mechanical work, they are not precise. Attempts to make this notion precise in the context of single phase continuum mechanics have led to controversy, although there is a measure of agreement about many of the results which emerge from the restrictions. Most trouble seems to center on the concept of entropy, even though none of the above statements involve entropy or appear to lead to its existence, except in special cases. In recent years, some workers in continuum mechanics have postulated the existence of a scalar field, called entropy, the production of which is restricted by the Clausius-Duhem inequality, and this is regarded as representing the second law of thermodynamics. With the help of this inequality restrictions are placed on constitutive equations, and some of these restrictions do seem to embody concepts contained in statements such as (A), (B) or (C). However, the approach based on the C-D inequality has certain shortcomings which have already been mentioned in section 1.

Before proceeding further, we recall that a <u>state of the body</u> (or its part $S \subseteq \mathcal{B}$) at time t is described by the position vector x and the temperature θ throughout the body together with the constitutive response functions for the fields (13). Once the response functions are given, we can then calculate the values of $E, K, \overline{w}$ and w_2 in (24) and (25). A <u>thermomechanical process</u>, or simply a <u>process</u>, is a time sequence of states; it is a continuous oriented curve in the space of states. Thus, a process may be defined by a sequence of values of θ, x throughout the body in the time interval $[0, \sigma]$. Similarly, the reverse process is defined by a sequence of values of θ, x throughout the body in the time interval $[\sigma, 2\sigma]$ subject to the conditions

$$\theta(t) = \theta(2\sigma - t) \quad , \quad x(t) = x(2\sigma - t) \quad . \tag{28}$$

The statements (A), (B) and (C) of the second law appear to involve different concepts: one is concerned with transformation of heat into mechanical energy being subject to definite limitations, while another deals with heat not being able to pass spontaneously from a body at lower temperature to one at higher temperature. In our discussion of the second law, we separate the notion of recoverable work in dissipative materials from that of conduction of heat. With reference to the former, we consider now a mathematical statement of the notion that in a dissipative medium it is impossible to reverse completely a process in which mechanical energy is transformed into heat. To this end, we observe that in any process the work done by the external mechanical forces acting on S is positive or negative depending on whether the external work is supplied to, or is withdrawn from S. In general, some of the work done results in a change of the kinetic and internal energies represented by the first two terms on the right-hand side of $(22)_2$, each of which may be positive, negative or zero. Also, part of the work done may be positive with a corresponding extraction from S as heat, or negative with a corresponding absorption of heat by S.

As already noted in section 4, for an elastic body $w_2 = 0$, and the different contributions to w defined by (22) will vary in sign depending on the process and will not be restricted to be either positive or negative for all processes. Consider any smooth process in the time interval $[0, \sigma]$, starting from rest with $v(0) = o$ and ending at rest with $v(\sigma) = o$. Then, for its reverse process in the time interval $[\sigma, 2\sigma]$, we also have $F(t) = F(2\sigma - t)$, $v(t) = -v(2\sigma - t)$ in view of (28). It follows that at the end of the process and its reverse process $\Delta\theta = 0$, $\Delta x = o$, $\Delta F = 0$, $\Delta v = o$ and hence for an elastic body, $\Delta\epsilon = 0$, $\Delta\eta = 0$, $\Delta\xi = 0$, $\Delta\Gamma = o$, $\Delta q = o$, $\Delta E = 0$,

$\Delta K = 0$, so that the body has returned to its original state. Then, all the work done in the process is recovered as work in the reverse process[10]. This recovery of work would not be possible if in every arbitrary process part of w always has a positive sign, since this part of w would then yield positive work both in the process and the reverse process.

With this motivation for recoverable work in a process, we assume that for any arbitrary process in a dissipative material only part of the work done is recoverable as work, the rest being transformed into heat. We therefore assume that in every process part of the work done is always nonnegative. Then, if at the end of any process and its reverse process the body has returned to the same state[11], some of the work done is always transformed into heat. Recalling that $w_2 = 0$ in (22) in the case of an elastic material for all processes, we interpret the above assumption for a dissipative material as

$$w_2 \geqq 0 \tag{29}$$

for all material parts $\mathcal{S}$ and all thermomechanical processes. Since t_1, t_2 in the time interval $\mathcal{I}$ are arbitrary and since ρw^* has already been assumed to be continuous, it follows that $\int_P \rho w^* dv \geqq 0$ for all arbitrary P. Hence, it follows from (29) that[12]

$$w^* \geqq 0 \ . \tag{30}$$

The procedure of section 3 and the thermodynamical inequality (30) have been applied by Green and Naghdi to a viscous fluid and to materials with fading memory [1, Secs. 5,6] and to elastic-plastic materials [14]. Also, Green and Naghdi [2] have studied the implications of the inequality (30) in regard to the classical statements of the second law of thermodynamics associated with cyclic thermomechanical processes. In particular, in [2, Sec. 4] attention is called to the fact that for some materials, such as a general viscoelastic material or an elastic-plastic material of the type discussed in [14], the usual four statements for cyclic motions associated with the second law are not applicable.

We now supplement the proposed inequality (30) with two further inequalities which stem from the statement (C) above. As in [1], consider first only the heat flux response in equilibrium cases for which heat flow is steady. By equilibrium, we mean that

$$\underset{\sim}{v} = \underset{\sim}{o} \ , \quad \dot{\underset{\sim}{F}} = \underset{\sim}{0} \ , \quad \dot{\theta} = 0 \quad \text{for all } t \ ,$$

where $\underset{\sim}{F}$ and θ, as well as all other relevant functions, are independent of t (but may depend on $\underset{\sim}{x}$). For these equilibrium cases, we adopt the

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[10] If work is extracted in the process, then it is absorbed by the body in the reverse process.

[11] In this case, a process and its reverse process together constitute a special type of cyclic process.

[12] The inequality (29) was first proposed in [2]. Previously, in [1, Sec. 4], a different mathematical interpretation of the same statement of one version of the second law was given in which E in (22) was replaced by $E'(P) = \int_P \rho \epsilon' dv$ and w^* in (26) by w in (27). For a wide variety of materials in which $\epsilon = \epsilon'$ the two conditions coincide.

classical heat conduction inequality

$$-\underset{\sim}{q} \cdot \underset{\sim}{g} \geqq 0 \tag{31}$$

for all time-independent temperature fields. We recall that when q is parallel to the temperature gradient $\underset{\sim}{g}$, (31) implies that heat flows in the direction of decreasing temperature.

For many materials of interest, the thermomechanical response of the medium is characterized in terms of certain kinematic and thermal variables (such as $\underset{\sim}{F}$ and θ) and their gradients but not their rates. In such cases, once the heat flux response function has been restricted by (31), the resulting conditions remain valid for all values of kinematic and thermal variables and not just the time-independent ones.

To obtain the second inequality mentioned above, let the continuum be in the state of rest with $\underset{\sim}{v} = \underset{\sim}{o}$ for all time and with the deformation gradient $\underset{\sim}{F}$ everywhere constant for all time. Then, $\underset{\sim}{D} = \underset{\sim}{O}$ everywhere and it follows from $(4)_1$ that ρ is independent of t. In addition, we restrict the temperature field to be spatially homogeneous so that $\theta = \theta(t)$. Keeping these in mind, from a combination of $(8)_1$ and $(8)_3$ we have

$$\rho r - \operatorname{div} \underset{\sim}{q} = \rho \dot{\varepsilon} \quad . \tag{32}$$

Since $\underset{\sim}{v} = \underset{\sim}{o}$ everywhere, no mechanical work is supplied to the body. Then, using (32) and (23), the external heat supplied to a part $\mathcal{S}$ of the body during the time interval $[t_1, t_2]$ is

$$\mathcal{H} = \Delta E(\mathcal{P}) \quad . \tag{33}$$

We now suppose that the body has been in thermal equilibrium during some period up to the time t_1 with constant internal energy ε_1 and constant temperature θ_1. We then assume that whenever heat is continually _supplied_ to a part $\mathcal{P}$ according to (33), the temperature $\theta(t)$ throughout the part will be increased, i.e.,

$$\Delta \theta > 0 \quad \text{whenever} \quad \mathcal{H} > 0 \quad . \tag{34}$$

Further, assuming suitable continuity, it follows from (33) and (34) that

$$\Delta \theta > 0 \quad \text{whenever} \quad \Delta \varepsilon > 0 \tag{35}$$

for all $t_2 > t_1$.

6.   Concluding remarks

The main differences between the recent approach to thermomechanics of single phase continua proposed by Green and Naghdi [1,2] and that based on the use of the C-D inequality are: (a) The introduction of a balance of entropy (6), along with the use of the energy equation as an identity for all thermomechanical processes; (b) a mathematical interpretation of a statement of the second law leading to the inequality (30), which represents the notion that in a dissipative medium it is impossible to reverse completely a process in which mechanical energy is transformed into heat; and (c) a restriction on change of temperature from equilibrium upon the addition of heat [see (35)] to accompany the classical restriction on the heat flux vector.

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Several criticisms of the use of the C-D inequality were cited in section 1. One of these by Day [7] arises from consideration of an initial boundary-value problem for the determination of the temperature field in a rigid heat conductor with memory. He shows that the value of entropy is not unique even though the internal energy and the heat conduction vector are uniquely determined. As already noted in [1], Day's criticism does not apply to the developments presented here.

We now make some observations regarding the procedure proposed in [1,2]. First, we recall that the field equations resulting from momentum balance involve only the mechanical response functions while that obtained from balance of energy involves both the thermal and the mechanical responses. In the traditional developments of thermomechanics, after the specification of constitutive equations, the former field equations yield a system of differential equations for the determination of deformation while the latter is regarded as a differential equation for the determination of temperature, after elimination of the external body force with the use of the local equations of motion[13]. In contrast, the development of Green and Naghdi [1,2] is such that the balance of entropy, which involves only the thermal responses, provides the differential equation for the temperature in parallel with the fact that the differential equations for the deformation are derived from the balance of momentum. Consistent with this, the energy equation (after the elimination of the external body force and the external heat supply) is employed as an identity for all thermomechanical process; and, hence, it does not yield any new differential equation for temperature or deformation. It is noteworthy that the energy equation as used here provides all the essential results — other than those arising from inequalities — concerning the relationships between the constitutive response functions or functionals prior to any appeal to a second law of thermodynamics. In this sense, the inequality (30) has been assigned a more subdued role relative to those of the conservation laws; and, in the main, this has been the spirit of the contents of [1,2] in regard to the type of restrictions which arise from an appropriate form of the second law of thermodynamics.

Acknowledgment

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[13]It is understood that the differential equation for temperature, as well as those for deformation, contain also coupled terms.

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This paper summarizes the recent work of Green and Naghdi [1,2] concerning the thermomechanics of dissipative materials, the main features of which are: (a) The introduction of a conservation law for entropy which holds for all materials, (b) the use of the energy equation as an identity for all processes, thereby leading to restrictions on constitutive equations, and (c) the development of an inequality representing a mathematical interpretation of a statement of the second law of thermodynamics.

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